Neutral and cationic alkyl and alkynyl complexes of lanthanum

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Neutral and Cationic Alkyl and Alkynyl Complexes of Lanthanum: Synthesis, Stability, and Cis-Selective Linear Alkyne Dimerization

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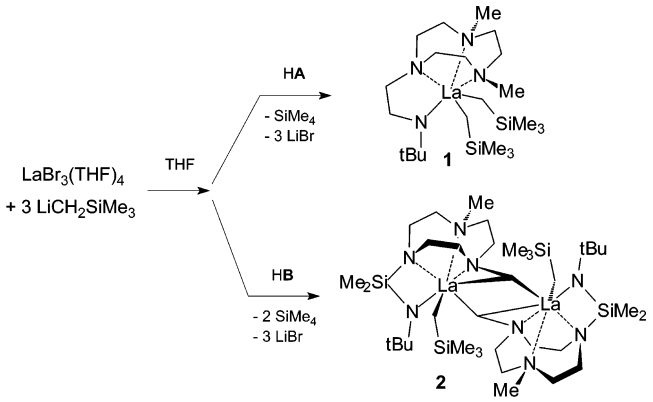
Summary: Neutral triazacyclononane−amide lanthanum dialkyl and dialkynyl complexes were synthesized and structurally characterized. A cationic triazacyclononane−amide lanthanum monoalkyl species was generated and found to be highly active (tof > 100 h^{-1}) in the rare cis-selective catalytic linear dimerization of phenylacetylene.

The chemistry of cationic group 3 metal and lanthanide alkyl complexes is still in its infancy, compared to that of the transition metals. The latter have been intensively investigated, especially because of their high activity in catalytic olefin polymerization.[1] The recent progress made in the synthesis of cationic group 3 metal and lanthanide alkyl complexes has exclusively focused on the metals for which the metal trialkyl species $M(CH_2SiMe_3)_3(THF)_n$ ($n = 2, 3$) are available as precursors: i.e., for the smaller metals from the series (group 3 metals Sc and Y and lanthanides ranging from Lu to Tb).[2−6] In contrast, only one isolated example, {(η^5-C_5Me_5)La[$CH(SiMe_3)_2$]}[BPh_4], was reported for the largest lanthanide metal, lanthanum.[7] Here we describe the convenient synthesis of neutral lanthanum dialkyl complexes with tetradentate monoanionic 1,4,7-triazacyclononane−amide (TACN-amide) ancillary ligands using an in situ peralkylation reaction of $LaBr_3(THF)_4$, followed by addition of the triazacyclononane−amine. The stability of the resulting dialkyl species depends strongly on the bridge between the TACN and amide ligand moieties. A cationic (TACN-amide)lanthanum monoalkyl species was generated and found to be a highly active catalyst for the unusual cis-selective linear dimerization of phenylacetylene.

Scheme 1



The ligands *N-tert*-butyl-2-(4,7-dimethyl[1,4,7]triazanon-1-yl)ethylamine (H**A**) and *N-tert*-butyl(4,7-dimethyl-[1,4,7]triazanon-1-yl)dimethylsilylamine (H**B**) were both prepared by starting from the known 4,7-dimethyl-1,4,7-triazacyclononane,[8] either by reaction with *N-tert*-butylchloroacetamide and subsequent reduction with $LiAlH_4$ (for H**A**)[4a] or by lithiation of the amine followed by reaction with (*tert*-butylamino)dimethylchlorosilane (for H**B**).

Reaction of $LaBr_3(THF)_4$ with 3 equiv of Me_3SiCH_2-Li in THF at ambient temperature for 3 h, followed by addition of 1 equiv of H**A** and subsequent extraction with and crystallization from pentane, afforded analytically pure crystalline [η^3:η^1-Me_2TACN$(CH_2)_2$N*t*Bu]La-$(CH_2SiMe_3)_2$ (**1**) in 44% isolated yield (Scheme 1).[9] The

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(9) Synthesis of **1**: at ambient temperature, solid $LiCH_2SiMe_3$ (0.28 g, 3.0 mmol) was added to a suspension of $LaBr_3(THF)_4$ (0.67 g, 1.0 mmol) in THF (60 mL). The solution was stirred for 3 h, after which Me_2-TACN−$(CH_2)_2NHBu^t$ (H**A**, 0.25 g, 1.0 mmol) was added. After the mixture was stirred for 3 h more, the volatiles were removed in vacuo. The mixture was extracted with pentane (2 × 50 mL), and the obtained extract was concentrated to 20 mL and cooled (−30 °C), yielding crystalline **1** (0.25 g, 0.44 mmol, 44%). ^{1}H NMR (500 MHz, 25 °C, C_6D_6): δ 3.08 (m, 2 H, NCH_2), 2.82 (m, 2H, NCH_2), 2.40−2.35 (m, 2 H, NCH_2), 2.27 (s, 6 H, NMe_2), 2.17−2.13 (m, 4 H, NCH_2), 1.79−1.74 (m, 2 H, NCH_2), 1.71−1.66 (m, 3 H, NCH_2), 1.44 (s, 9 H, Bu^t), 0.46 (s, 18 H, $SiMe_3$), −0.66 (d, J = 10.5 Hz, 2 H, $LaCH_2Si$), −0.80 (d, J = 10.5 Hz, 2 H, $LaCH_2Si$). ^{13}C NMR (125.7 MHz, 25 °C, C_6D_6): δ 59.7 (t, J = 132 Hz, NCH_2), 55.7 (t, J = 135 Hz, NCH_2), 54.9 (s, Bu^t C), 54.3 (t, J = 133 Hz, NCH_2), 52.1 (t, J = 130 Hz, NCH_2), 48.1 (t, J = 104 Hz, $LaCH_2$), 47.5 (t, J = 128 Hz, NCH_2), 47.0 (q, J = 135 Hz, NMe), 30.2 (q, J = 123, Bu^t Me), 5.2 (q, J_{CH} = 116 Hz, $SiMe_3$). Anal. Calcd for $C_{22}H_{53}N_4LaSi_2$: C, 46.46; H, 9.39; N, 9.85; Found: C, 45.90; H, 9.21; N, 9.76.

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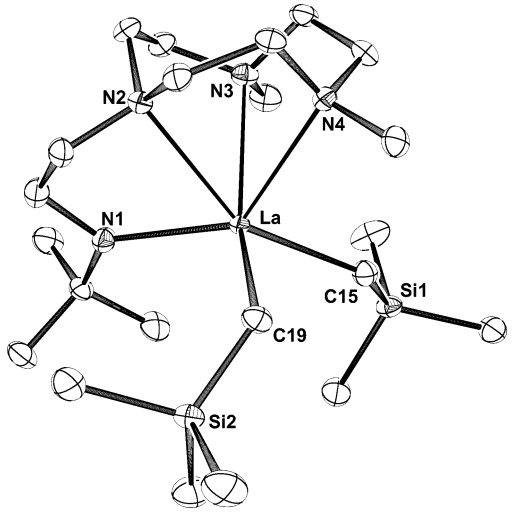


Figure 1. Molecular structure of [Me_2TACN(CH_2)$_2$N*t*Bu]-La(CH_2SiMe_3)$_2$ (**1**), with 50% probability ellipsoids. Selected interatomic distances (Å) and angles (deg): La−C(15) = 2.632(2), La−C(19) = 2.618(2), La−N(1) = 2.348(2), La−N(2) = 2.720(2), La−N(3) = 2.783(2), La−N(4) = 2.754(2); N(1)−La−N(2) = 68.60(7), C(15)−La−C(19) = 99.41(8), N(3)−La−C(19) = 147.74(7), N(4)−La−C(15) = 95.42(8), La−C(15)−Si(1) = 142.4(1), La−C(19)−Si(2) = 126.2(1).

complex was characterized by single-crystal X-ray diffraction,[10] and its molecular structure is shown in Figure 1. The metal center has a distorted-octahedral coordination geometry, with the three amine nitrogens of the TACN moiety capping a trigonal face. There is considerable asymmetry in the N(1)−La−C(alkyl) angles: 127.12(8)° for C(15) and 104.68(7)° for C(19). This may be associated with minimizing the steric interference between the alkyl groups and the methyl substituents on the TACN moiety. Nevertheless, room-temperature NMR spectra of **1** are consistent with an averaged C_s symmetry, and only at significantly lower temperatures is a broadening of the resonances observed, associated with the interconversion between the two asymmetric conformers. Thus, for La the TACN-amide dialkyl complex is much more flexible than for the smaller metal Y, where the slow-exchange limit is already reached at around 0 °C at the same spectrometer frequency.[4a]

Performing the same reaction sequence described above, but now using 1 equiv of the TACN-amine H**B** (Scheme 1), resulted in the isolation in moderate yield (62% of crude material, 17% after recrystallization) of a product that was characterized by single-crystal X-ray diffraction[11] as the dinuclear {[Me(μ-CH_2)TACN-($SiMe_2$)N*t*Bu]La(CH_2SiMe_3)}$_2$ (**2**; Figure 2). This product is the result of the metalation of one of the methyl substituents on the TACN ligand moiety, with concomitant formation of $SiMe_4$ and subsequent dimerization. It is isolated as the sole organometallic product even

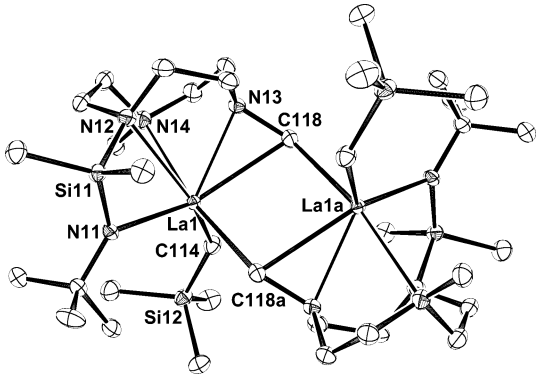


Figure 2. Molecular structure of {[Me(μ-CH_2)TACN-($SiMe_2$)N*t*Bu]La(CH_2SiMe_3)}$_2$ (**2**), with 50% probability ellipsoids. Only one of the two independent molecules in the unit cell is shown. Selected interatomic distances (Å) and angles (deg): La(1)−C(114) = 2.627(2), La(1)−C(118) = 2.747(2), La(1)−C(118a) = 2.803(2), La(1)−N(11) = 2.425(2), La(1)−N(12) = 2.788(2), La(1)−N(13) = 2.518(2), La(1)−N(14) = 2.890(2), N(13)−C(118) = 1.488(3); N(11)−La(1)−N(12) = 60.16(5), C(118)−La(1)−C(118a) = 83.95(6), La(1)−C(118)−La(1a) = 96.05(6), La(1)−C(114)−Si(12) = 135.1(1).

when the reaction is performed at −10 °C. In contrast, compound **1** with the $(CH_2)_2$ bridge is stable at ambient temperature in C_6D_6 solution for at least 1 day, as seen by NMR spectroscopy. This indicates that the nature of the bridging moiety in the TACN-amide ligand has a profound effect on the thermal stability of the (TACN-amide)La(CH_2SiMe_3)$_2$ derivatives. In **2**, the two La centers are bridged by the methylene group resulting from the NMe deprotonation. The La_2C_2 diamond is not quite equilateral (with the shortest La−C distance to the metal that carries the NCH_2 functionality), and the La−N distance to the nitrogen with the CH_2 group is significantly shorter than the other La−N(amine) distances. The N−CH_2 distance is normal for a N−C single bond. The N(amide)−La−N(bridgehead) angle in **2** of 60.16(5)° is noticeably smaller than the 68.60(7)° angle in **1**, and this reduction of the ligand bite angle is the likely source of the instability of the dialkyl complex with the $SiMe_2$ bridge. NMR spectroscopy indicates the presence in solution of two isomers of **2**, in a 3:1 ratio. These isomers possibly derive from cis−trans isomerism relative to the central La_2C_2 diamond. The methylene protons of the $SiCH_2$ and NCH_2 groups are diastereotopic; the resonances of the former are located at δ −0.62 and −0.94 ppm ($^2J_{HH}$ = 11.0 Hz) and the latter at δ 2.77 and 1.49 ppm ($^2J_{HH}$ = 13.5 Hz) in the major isomer.

The dialkyl complex **1** reacts with 2 equiv of phenylacetylene to generate the moderately soluble dinuclear dialkynyl complex {[Me_2TACN(CH_2)$_2$N*t*Bu]La(CCPh)-(μ-CCPh)}$_2$ (**3**) and 2 equiv of $SiMe_4$. A crystal structure determination[12] of **3** (Figure 3) revealed a twisted cis-type arrangement of the TACN-amide ligands around a central La(μ-CCPh)$_2$La core that is somewhat puckered, as seen from the dihedral angle C(53)−La(1)−C(23)−La(2) of −20.07(6)°. The μ-alkynyl groups are bridging the metal centers in an asymmetric fashion,

(10) Crystal data for **1**: $C_{22}H_{53}LaN_5Si_2$, space group $P2_1/n$, monoclinic, a = 8.5787(3) Å, b = 17.6777(7) Å, c = 19.8289(9) Å, β = 99.498(1)°, V = 2965.9(2) Å^3; T = 100(1) K, Z = 4, μ(Mo Kα) = 15.35 cm^{-1}, 20 516 reflections measured (6852 unique), final refinement converged at $R_w(F^2)$ = 0.0676 with 474 parameters.

(11) Crystal data for **2**·C_7H_8: ($C_{18}H_{43}LaN_4Si_2$)$_2$·C_7H_8, space group $P\bar{1}$, triclinic, a = 10.8289(4) Å, b = 12.8117(5) Å, c = 20.3165(8) Å, α = 91.104(1)°, β = 93.765(1)°, γ = 97.498(1)°, V = 2787.44(19) Å^3; T = 100(1) K, Z = 4, μ(Mo Kα) = 16.32 cm^{-1}, 26 514 reflections measured (13 308 unique), final refinement converged at $R_w(F^2)$ = 0.0570 with 868 parameters.

(12) Crystal data for **3**·1.5C_7H_8: ($C_{30}H_{41}LaN_4$)$_2$.1.5C_7H_8, space group $P\bar{1}$, triclinic, a = 14.3298(7) Å, b = 16.0756(8) Å, c = 16.8773(8) Å, α = 99.229(1)°, β = 111.439(1)°, γ = 94.851(2)°, V = 3528.4(3) Å^3; T = 100(1) K, Z = 2, μ(Mo Kα) = 12.37 cm^{-1}, 32 332 reflections measured (16 750 unique), final refinement converged at $R_w(F^2)$ = 0.0842 with 1054 parameters.

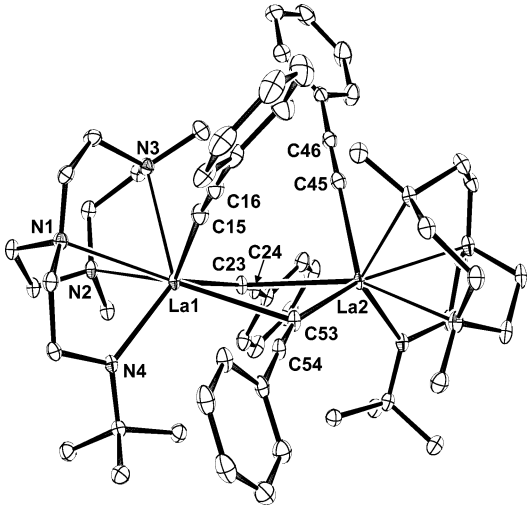
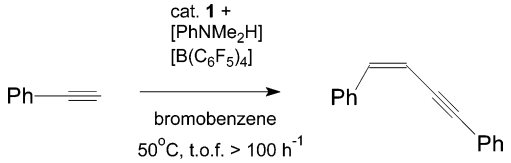


Figure 3. Molecular structure of {[$Me_2TACN(CH_2)_2NtBu$]-La(CCPh)(μ-CCPh)}$_2$ (**3**), with 30% probability ellipsoids. Selected interatomic distances (Å) and angles (deg): La(1)−C(15) = 2.674(2), La(2)−C(45) = 2.655(2), La(1)−C(23) = 2.698(2), La(2)−C(23) = 2.876(2), La(1)−C(53) = 2.855(2), La(2)−C(53) = 2.705(2), La(1)−N(1) = 2.702(2), La(1)−N(2) = 2.867(2), La(1)−N(3) = 2.756(2), La(1)−N(4) = 2.365(2), C(15)−C(16) = 1.226(3), C(23)−C(24) = 1.221(3); La(1)−C(15)−C(16) = 174.3(2), La(1)−C(23)−C(24) = 160.9(2), La(2)−C(23)−C(24) = 95.5(2).

with La(1)−C(23) = 2.698(2) Å and La(1)−C(23)−C(24) = 160.8(2)° vs La(2)−C(23) = 2.876(2) Å and La(2)−C(23)−C(24) = 95.5(2)°. This type of bridging mode is similar to that found in lanthanidocene μ-alkynyl dimers.[13] There is no significant difference in C≡C bond length between the bridging and terminal alkynyl ligands. The ^{13}C NMR spectrum of **3** shows two resonances (at δ 163.9 and 161.2 ppm) for the La-bound alkynyl carbons.

Reaction of the dialkyl complex **1** with the Brønsted acid [$PhNMe_2H$][$B(C_6F_5)_4$] in both C_6D_5Br/d_8-THF and C_6D_6/d_8-THF solvent mixtures was seen by ^{1}H and ^{13}C NMR to generate $SiMe_4$, free $PhNMe_2$, and an alkyl species, likely to be {[η^3:η^1-$Me_2TACN(CH_2)_2NtBu$]La-(CH_2SiMe_3)(d_8-THF)$_x$}[$B(C_6F_5)_4$] (**4**).[14] As was observed for the analogous Y species,[4a] the ^{13}C NMR Ln−CH_2 resonance in cationic **4** (δ 55.4 ppm in C_6D_6/d_8-THF) is found downfield from that in the neutral dialkyl precursor **1** (δ 47.9 ppm in the same solvent). The reaction of the dialkynyl species **3** with [$PhNMe_2H$][$B(C_6F_5)_4$] and the reaction of the ionic La alkyl **4** with 1 equiv of phenylacetylene (in C_6D_5Br/d_8-THF solvent) both lead to the formation of a poorly soluble product, visible as an orange oily precipitate in the NMR tube. In the reaction of the dialkynyl compound, it was observed by ^{1}H NMR that the phenylacetylene liberated in the initial reaction of **3** with the Brønsted acid is rapidly converted into *cis*-1,4-diphenylbut-1-en-3-yne.[15]

Scheme 2



Neutral lanthanide metallocene species are known to catalyze the dimerization of terminal alkynes to give predominantly the linear head-to-head enyne dimer with a trans configuration around the enyne double bond.[17] Formation of *trans*-enyne is readily explained by 2,1-insertion of the alkyne into the metal−alkynyl bond, followed by product release via alkyne deprotonation. Recently, Hou et al. demonstrated that neutral cyclopentadienyl−amide lanthanide species catalyze the linear dimerization of terminal alkynes with high selectivity for the *cis*-enyne product.[18] The cationic {[η^3:η^1-$Me_2TACN(CH_2)_2NtBu$]La(CH_2SiMe_3)}$^+$ species is also able to catalyze this rare reaction with high selectivity (Scheme 2), but at a much faster rate. In reactions performed at 50 °C on an NMR tube scale with **1**/[$PhNMe_2H$][$B(C_6F_5)_4$] and 45 or 450 equiv of phenylacetylene in 0.4 mL of C_6D_5Br solvent, full conversion was reached (in 15 and 240 min, respectively; the relatively slow conversion in the latter experiment may be due to the low polarity of the medium at high substrate concentration). Combined NMR and GC/MS characterization of the products revealed a high selectivity for *cis*-1,4-diphenylbut-1-en-3-yne (99% of the dimer fraction), with a small amount of trimers of the alkyne as side product (≤1%; multiple isomers, as seen by GC/MS).

In conclusion, we have shown that lanthanum dialkyl complexes with triazacyclononane−amide ancillary ligands can conveniently be synthesized directly from $LaBr_3(THF)_4$ via an in situ alkylation procedure followed by addition of the ligand. These species, and their cationic monoalkyl derivatives, should thus readily be available for all the group 3 and lanthanide metals, allowing a comparison of their behavior as a function of the metal ionic radius. The cationic TACN-amide lanthanum hydrocarbyl system provides a highly active and selective catalyst for the dimerization of phenylacetylene to *cis*-1,4-diphenylbut-1-en-3-yne. The source of the selectivity for the *cis*-enyne product is as yet unclear. The mechanism proposed by Yi et al. for (C_5Me_5)$Ru(PPh_3)H_3$-catalyzed formation of this product[16] involves a vinylidene intermediate and is unlikely to play a role here, whereas Eisen et al. proposed an isomerization of an intermediate insertion product to explain *cis*-enyne formation in [$(Et_2N)_3U$][BPh_4]-catalyzed alkyne conversions.[19] In contrast, for the high

(13) See e.g.: Atwood, J. L.; Hunter, W. E.; Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1981**, *20*, 4115.

(14) Data for **4** are as follows. ^{1}H NMR (300 MHz, 20 °C, C_6D_6/ THF-d_8): δ 2.91 (m, 2 H, NCH_2), 2.61 (m, 2 H, NCH_2), 2.20 (m, 4 H, NCH_2), 2.11 (s, 6 H, NMe), 1.75 (m, 4 H, NCH_2), 1.28 (s, 9 H, Bu^t), 0.42 (s, 9 H, $SiMe_3$), −0.82 (br, 2 H, $LaCH_2Si$). ^{13}C{^{1}H} NMR (75.4 MHz, 20 °C, C_6D_6/THF-d_8): δ 60.0 (NCH_2), 55.4 (NCH_2), 55.4 ($LaCH_2Si$), 54.7 (s, Bu^t C), 53.7 (NCH_2), 52.6 (NCH_2), 47.0 (NMe), 45.2 (NCH_2), 29.7 ($NCMe_3$), 4.3 ($LaCH_2SiMe_3$). Data for the anion are omitted.

(15) As indicated by the characteristic ^{1}H NMR doublet resonances for *cis*-PhC*H*=C*H*C≡CPh at δ 6.52 and δ 5.89 with $^3J_{HH}$ = 11.7 Hz (C_6D_5Br/d_8-THF solvent).[16]

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selectivity of the catalysis by neutral cyclopentadienyl−amide lanthanide systems, Hou et al. invoked a mechanism involving a bimetallic active species.[18] The observation that the generation of cationic TACN-amide lanthanum acetylide species, either from **2** or from **4**, results in the formation of a poorly soluble organometallic product (even in bromobenzene/THF mixtures) might be an indication that a dinuclear species is formed. In this case, this is likely to be dicationic, and such a compound is expected to be relatively poorly soluble. The nature of this species and its behavior are the subjects of current investigations.

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Supporting Information Available: Text giving full experimental characterization data for H**B** and **1**−**4** and tables of crystal data, structure solution and refinement details, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1**−**3** as well as details of catalytic phenylacetylene dimerization experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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